by the experimental result. As can be seen from the packing diagram of Fig. 2, there are no significantly short distances in (III) between neighboring Br atoms [the shortest intermolecular distance is 5·63 (1) Å, involving Br(1) and Br(2)]. The shortest intermolecular distances involving F and Br atoms are 3·06 (1) Å [Br(1) and F(1)] and 3·20 (1) Å [Br(2) and F(2)] while the predicted sum of the van der Waals radii for fluorine and bromine is 3·32 Å (Bondi, 1964). Compounds (I) and (III) are isostructural nonetheless with all interhalogen contacts in (III) involving F and Br atoms. Thus, the close Br···Br contacts in (I) may be stabilizing interactions but they apparently are not structure determining because substitution of an F atom for one of the Br atoms does not alter the packing pattern.

References

BIELUSHKIN, A. V., NATKANIEC, I., WASICKI, J., KHOMENKO, V. G., TELEZHENKO, YU. & WASIUTYNSKI, T. (1986). 10th Eur. Crystallogr. Meet. Wroclaw, Poland. Collected Abstracts, 3A-05, pp. 350–351.

BONDI, A. (1964). J. Phys. Chem. 68, 441–451.

BROCK, C. P. (1980). Acta Cryst. B36, 968–971.

BROCK, C. P. & MINTON, R. P. (1989). J. Am. Chem. Soc. 111, 4586–4593.

BROWN, F., LOW, J. N. & TOLLIN, P. (1986). J. Appl. Cryst. 19, 410.

CASALONE, G., MARIANI, C., MUGNOLI, A. & SIMONETTA, M. (1969). Acta Cryst. B25, 1741–1750.

Enraf–Nonius (1982). Structure Determination Package. Enraf–Nonius, Delft, The Netherlands.

KITAIGORODSKY, A. I. (1973). Molecular Crystals and Molecules. New York: Academic Press.

KRONEBUSCH, P., GLEASON, W. B. & BRITTON, D. (1976). Cryst. Struct. Commun. 5, 17–20.

LEMÉE, H. M., TOUPET, L., DÉLUGEARD, Y., MESSAGER, J. C. & CAILLEAU, H. (1987). Acta Cryst. B43, 466–470.

McKINNEY, J. D. & SINGH, P. (1988). Acta Cryst. C44, 558–562.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). Acta Cryst. A24, 351–359.

SAITO, K., ATAKE, T. & CHIHARA, H. (1987). Acta Cryst. B43, 383–385.

Structure of Thialysine Hydrochloride

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Abstract. 2-Ammonio-3-[(2-ammonioethyl)thio]propionate chloride, $C_5H_{13}N_2O_2S^+.Cl^-$, $M_r = 200.7$, monoclinic, $P2_1$, $a = 5.1275$ (4), $b = 7.897$ (1), $c = 11.208$ (1) Å, $\beta = 104.129$ (8)°, $V = 440.1$ Å^3, $Z = 2$, $D_x = 1.519$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 6.12$ cm^{-1}, $F(000) = 212$, $T = 295$ K, final $R = 0.021$, $wR = 0.027$ for 784 reflections with $I > 3\sigma(I)$. The two ammonium cations form seven hydrogen bonds: α-NH$_3^+$ acts as a donor for three carboxylate O atoms and one Cl$^-$ ion whereas ε-NH$_3^+$ is linked to three Cl$^-$ ions.

Introduction. The alteration of one or more aminoacid residues in a macromolecule is a well established procedure for investigating the influence of the residue(s) on structure and function. The changes, which are introduced by site-directed mutagenesis, are limited to those specified by the genetic code. With these restrictions, for example, it is not possible to replace lysine with a residue in which the distance

between the α- and ε-amino groups has been changed, or to introduce such an altered lysine residue at another location in the polypeptide. The insertion of a thialysine (I) residue might be achieved by the introduction of cysteine with the usual procedures followed by the reaction of the cysteine-containing macromolecule with ethylenimine to convert the cysteine to a thialysine. The structural properties of the Cα-linked chain in thialysine and a comparison with that in lysine was of primary interest in the investigation reported here.
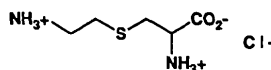
(I)

Experimental. Colorless crystals from aqueous ethanol; 0·2 × 0·35 × 0·4 mm crystal; CAD-4 diffractometer, graphite monochromator, cell parameters

Table 1. *Fractional coordinates and equivalent iso-tropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å²)
Cl	0.8772 (1)	0.3847	0.61177 (6)	2.55 (3)
S	0.2820 (1)	0.4449 (1)	0.30455 (6)	2.17 (3)
O1	0.2652 (4)	0.4986 (3)	-0.0350 (2)	2.43 (8)
O2	0.7116 (4)	0.5045 (3)	0.0402 (2)	2.68 (9)
N1	0.1707 (5)	0.7427 (4)	0.1113 (2)	1.9 (1)
N2	0.6374 (6)	0.1165 (4)	0.4013 (2)	2.3 (1)
C1	0.4739 (6)	0.5466 (4)	0.0385 (2)	1.8 (1)
C2	0.4474 (6)	0.6698 (4)	0.1405 (3)	1.7 (1)
C3	0.5245 (6)	0.5910 (4)	0.2679 (3)	1.9 (1)
C4	0.3308 (7)	0.2551 (4)	0.2219 (3)	2.4 (1)
C5	0.5965 (8)	0.1706 (5)	0.2710 (3)	2.5 (1)

Table 2. *Bond distances (Å), angles (°) and torsion angles (°) with e.s.d.'s in parentheses*

S—C4	1.811 (3)	N2—C5	1.487 (4)
S—C3	1.816 (3)	C1—C2	1.532 (4)
O1—C1	1.240 (3)	C2—C3	1.519 (4)
O2—C1	1.259 (4)	C4—C5	1.496 (5)
N1—C2	1.492 (4)		

C4—S—C3	102.9 (1)	N1—C2—C1	109.5 (2)
O1—C1—O2	127.2 (3)	C3—C2—C1	113.1 (3)
O1—C1—C2	118.1 (3)	C2—C3—S	115.9 (2)
O2—C1—C2	114.7 (2)	C5—C4—S	114.1 (2)
N1—C2—C3	112.3 (2)	N2—C5—C4	112.7 (3)

S—C4—C5—N2	60.2 (4)	O2—C1—C2—N1	166.1 (3)
S—C3—C2—N1	49.7 (3)	O2—C1—C2—C3	-67.9 (3)
S—C3—C2—C1	-74.9 (3)	C2—C3—S—C4	76.7 (2)
O1—C1—C2—N1	-14.4 (4)	C3—S—C4—C5	67.8 (3)
O1—C1—C2—C3	111.6 (3)		

Table 3. *Hydrogen-bond characteristics*

N—H···A	N···A (Å)	H···A (Å)	N—H (Å)	N—H···A (°)
N1—H4···O1'	2.979 (3)	2.50 (3)	0.97 (4)	110 (3)
N1—H4···O2"	2.832 (4)	1.94 (4)	0.97 (4)	152 (3)
N1—H3···O2'"	2.966 (4)	2.10 (5)	0.89 (5)	164 (3)
N1—H2···Cl⁻ⁱ	3.365 (3)	2.57 (4)	0.81 (3)	167 (3)
N2—H12···Cl⁻	3.185 (3)	2.31 (4)	0.87 (4)	162 (3)
N2—H11···Cl⁻ⁱᵛ	3.122 (3)	2.21 (4)	1.00 (4)	105 (3)
N2—H13···Cl⁻ᵛ	3.185 (3)	2.31 (4)	0.90 (4)	104 (3)

Symmetry codes: (i) $-x, \frac{1}{2}+y, -z$; (ii) $1-x, \frac{1}{2}+y, -z$; (iii) $-1 +x, y, z$; (iv) $2-x, -\frac{1}{2}+y, 1-z$; (v) $1-x, -\frac{1}{2}+y, 1-z$; (vi) $1 -x, \frac{1}{2}+y, 1-z$.

from 25 reflections automatically centered in the range $10.4 < \theta < 18.4°$, $2\theta–\theta$ scan at variable θ speed of 1.03 to 8.24° min⁻¹; six standard reflections measured every 2 h, intensity variation of −9.4–1.2%, −2.7% average, decay correction applied; each scan recorded in 96 steps over the range of $1.5(0.85 + 0.35\tan\theta)°$ and processed subsequently with a modified Lehmann–Larsen procedure (Lehmann & Larsen, 1974; Ammon, 1986); $\theta_{max} = 25°$, 934 reflections measured, 839 unique reflections, 784 with $I > 3\sigma(I)$, $R_{int} = 0.005$ for 95 common reflections; index range for $h, k, l = 0$ to 6, 0 to 9, −12 to 12; no absorption correction. All crystallographic calculations performed with the *TEXSAN* program system (Molecular Structure Corporation, 1985) on a DEC

MicroVAX II computer; structure solved with the *MITHRIL* (Gilmore, 1983) link incorporated in *TEXSAN*. Full-matrix least-squares refinement, atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 155–175); anisotropic temperature factors for C, N, O and S atoms, individual isotropic term for H atoms, H-atom coordinates refined; $\Sigma w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, reflections with $I < 3\sigma(I)$ excluded from refinement; maximum Δ/σ of 0.049 in the final least-squares cycle. Final R, wR and S are 0.021, 0.027 and 1.26; minimum and maximum values in final $\Delta\rho$ map of −0.16 and +0.16 e Å⁻³. Atomic coordinates are listed in Table 1.* The *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display the *ORTEP* (Johnson, 1965) drawings on a VAX Station II monitor, add the atom labels and prepare print files for a Hewlett–Packard Laser-Jet II printer.
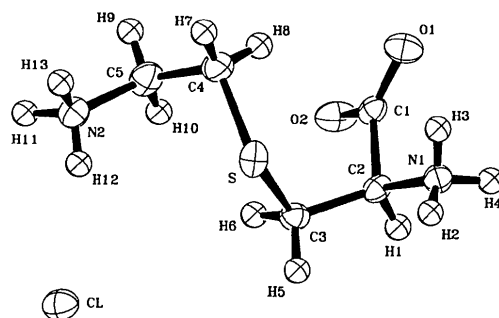

Fig. 1. An *ORTEP* diagram for thialysine hydrochloride. The C, O, N and Cl atoms are shown as 50% boundary ellipsoids; H atoms are drawn as spheres with $B = 1.5$ Å².
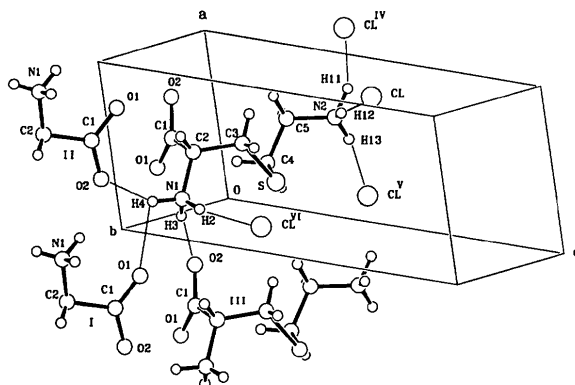

Fig. 2. An *ORTEP* diagram illustrating the scheme of hydrogen bonding in the thialysine hydrochloride structure.

Discussion. Bond lengths, bond angles and torsion angles are given in Table 2; an *ORTEP* (Johnson, 1965) drawing is shown in Fig. 1. The molecule is a diammonium carboxylate. The two ammonium cations are involved in a total of seven hydrogen bonds (Table 3, Fig. 2). H3 and H4 on the α-NH$_3^+$ participate in three H bonds to carboxylate O atoms; these interactions are listed on the first three lines in Table 3. Although these data and the packing diagram of Fig. 2 suggest that H4 forms a bifurcated hydrogen bond, the N1—H4···O1 contact is especially weak with an H···O distance of 2·50 (3) Å. The H4 bifurcation geometry is close to planar with a sum of 351·6 (4)° for the three angles at H4. The third H atom, H2, is linked to a chloride ion with a N···Cl$^-$ distance of 3·365 (3) Å. Each of the three ε-NH$_3^+$ group H atoms participates in an N—H···Cl$^-$ interaction. Each chloride ion is linked to four N-bonded H atoms in an approximately tetrahedral arrangement; the six H···Cl···H angles range from 94 to 124°.

It was expected that the C2···C5 distance in thialysine would be larger than the corresponding separation in lysine [L-lysine monohydrochloride dihydrate, (II); Koetzle, Lehmann, Verbist & Hamilton (1972)] because of C—S *vs* C—C bond-length differences: in (I), C—S = 1·816 (3) and 1·811 (3) Å; in (II), C—C = 1·529 and 1·535 Å. However, the observed C2···C5 distances in the two molecules are reversed with 4·209 (5) Å in thialysine and 5·118 Å in L-lysine. This apparent discrepancy may be accounted for by differences in the side-chain torsion angles. In thialysine, the C2—C3—S—C4 and C3—S—C4—C5 torsion angles are 76·7 (2) and 67·8 (3)°, compared to the corresponding C—C—C—C values of −175·1 nd 173·1° in lysine. A survey of the Cambridge Structural Database (1990) for the open-chain fragment CH—CH$_2$—S—CH$_2$—CH$_2$ was made to determine if there is a conformational preference for the C—C—S—C—C

unit. Values of the torsion angles corresponding to C2—C3—S—C4 and C3—S—C4—C5 were found to occur in two groups. Sixteen were in one group with a range of 59·2–87·0° (average = 77·3°) and four fell into a second group with a range of 152·0–177·4° (average = 170·2°). The corresponding C2···C5 distances were 3·71–4·77 Å (average = 4·30 Å) for the first group and 4·77–5·28 Å (average = 4·95 Å) in the second, a difference of about 0·6 Å. Thialysine can be seen to belong to the more common first group and lysine to the less common second group. Given these differences, one cannot predict with any level of confidence the C2···C5 separation of a thialysine residue in a macromolecule or the effect of the residue on the conformations in the local environment.

References

AMMON, H. L. (1986). *CAD4PROFILE*. Unpublished.
Cambridge Structural Database. (1990). June update. Cambridge Crystallographic Data Centre, Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.
GILMORE, C. J. (1983). *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures*. Univ. of Glasgow, Scotland.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
KOETZLE, T. F., LEHMANN, M. S., VERBIST, J. J. & HAMILTON, W. C. (1972). *Acta Cryst.* **B28**, 3207–3214.
LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.
LUO, J., AMMON, H. L. & GILLILAND, G. L. (1989). *J. Appl. Cryst.* **22**, 186.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Structure of Nortriptyline Hydrochloride

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Abstract. $C_{19}H_{22}N^+.Cl^-$, $M_r = 299·84$, monoclinic, $P2_1/c$, $a = 5·070$ (2), $b = 34·088$ (5), $c = 9·976$ (1) Å, $\beta = 90·74$ (2)°, $V = 1724·0$ Å^3, $Z = 4$, $D_x =$ 1·16 g cm^{-3}, λ(Mo $K\alpha_1$) = 0·70930 Å, $\mu = 2·2$ cm^{-1}, $F(000) = 640$, $T = 295$ K, final $R = 0·046$ for 1381 observed reflections. The nortriptyline molecule crys-